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Electrochemical Removal of Chloride Ions from Reinforced Concrete: Initial Evaluation of the Pier S19 Field Trial

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Abstract: The paper reports the initial evaluation of a commercial process for the electrochemical removal of chloride ions from concrete. A trial was conducted over an eight week period in 1989 on a section of Pier S19 of the Burlington Skyway. The evaluation included visual examination, corrosion potential and rate-of-corrosion measurements on the structure, and petrographic examination and the measurement of chloride ion profiles on samples removed from the structure.

Data up to thirteen months after treatment of the concrete are reported. The treatment was successful in moving chloride ions away from the reinforcing steel and in removing a substantial proportion from the concrete without apparent damage to the concrete. The long term effectiveness of the treatment is the major unknown factor.

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ELECTROCHEMICAL REMOVAL OF CHLORIDE IONS FROM REINFORCED CONCRETE: INITIAL EVALUATION OF THE PIER S19 FIELD TRIAL

INTRODUCTION

The feasibility of using electrochemical techniques to remove chloride ions from concrete, and thereby arrest or reduce corrosion of embedded reinforcement, was investigated in two major studies in the 1970's (1-3). The process consists of applying an anode and an electrolyte to the surface of a reinforced concrete structure and passing current between the anode and the reinforcing steel, which acts as a cathode. The technique is similar to the application of cathodic protection but differs in two important respects: the anode is temporary, and the current density applied is approximately one hundred times that used in most cathodic protection installations. However, if successful, the technique has the important advantage over cathodic protection in that it does not require regular monitoring and maintenance.

Although the studies performed by Battelle Columbus Laboratories (1,2) and the Kansas Department of Transportation (3) indicated that electrochemical migration of chloride ions was a promising rehabilitation technique, there was little further research in North America until the Strategic Highway Research Program (SHRP). This was largely because of concerns for undesirable effects on the concrete and steel such as an increase in permeability, reduction in bond of the reinforcement, migration of alkalis to the reinforcement, and the possibility of cracking because of high temperatures developed in the concrete. A project was defined within SHRP to examine these effects, determine the feasibility of electrochemical removal techniques, and, if feasible, develop procedures for use in the field (4). SHRP Contract C-102A, "Electrochemical Chloride Removal and

Protection of Bridge Components" was awarded in May 1988 with a completion date of March 1993. Preliminary findings indicated that the technique is feasible (5).

Work in Europe has led to the development of an electrochemical technique for the treatment of carbonated concrete and the removal of chloride ions. The treatment is known commercially as the NORCURE™ process. The purpose of the current study was to evaluate this process. The study was funded by the Ontario Ministry of Transportation but, because it was the first application in North America and was closely related to the SHRP study, the SHRP contractor was invited to audit the application (6). This paper describes the treatment of a section of Pier S19 at the Burlington Skyway in Ontario, during an eight-week period from July to September 1989 and the results of condition surveys up to October 1990.

FIELD PROCEDURES

Test Site

The test site was the lower 4 m of the west column of Pier S19 of the Burlington Skyway. The plan dimensions of the pier were approximately 1.7 m x 3.0 m and the area treated was approximately 30.8 m^2. The north face was left untreated to provide a control area. The column was relatively lightly reinforced, the surface area of reinforcement being approximately 0.55 m^2 per m^2 of concrete surface for the east and west faces, and 0.79 m^2 per m^2 of concrete surface for the north and south faces.

The piers of the Burlington Skyway were constructed in 1955. Roadway drainage, which contained salt in the winter months, flowing through open deck joints and

over portions of the piers had caused corrosion of the reinforcement even though the cover was generally in excess of 75 mm. The concrete contained approximately 330 kg/m³ of cement, a crushed dolomitic limestone coarse aggregate, and a natural sand fine aggregate. The water-cement ratio was about 0.45. The dolomitic limestone was high in chloride ion content with the result that the "background" concentration of chloride ion in the concrete was measured to be 0.042 percent by mass (using the acid-soluble extraction procedure). If the threshold value for corrosion of embedded reinforcement is taken to be 0.20 percent by mass of cement, the threshold value for the concrete in Pier S19 can be calculated to be 0.070 percent by mass of concrete.

Prior to commencing the electrochemical treatment, a condition survey was made of the test site. This included:

- a visual survey of the concrete surface
- a delamination survey by sounding
- measurement of concrete cover
- verification of electrical continuity of the reinforcement
- measurement of corrosion potentials
  (in accordance with ASTM C-876-87)
- corrosion rate measurements (using a commercial "3LP" device)
- removal of cores for petrographic examination and measurement of chloride ion content.

Four small graphite probes and two thermocouples were installed at the depth of the steel. A 220 V/30 A temporary electrical service was provided.

Installation

A connection was made to the reinforcement and insulated to prevent corrosion. Wooden strips, approximately 40 mm wide by 20 mm thick, were fastened vertically to the concrete using insulated anchor screws. Cellulose fiber, moistened with lime-water to act as an electrolyte, was sprayed on the concrete to the same thickness as the battens, as shown in Figure 1. A 100 x 100 mm (5 mm wire diameter) steel mesh was attached to the wooden strips with staples as shown in Figure 2, and a second layer of moist fiber applied to cover the mesh to a thickness of about 25 mm.

An electrical connection was made to the mesh on each face and insulated to reduce corrosion. The wires from the mesh were connected to the positive terminal of the rectifier and the wire from the reinforcement to the negative terminal. The power was switched on and, after fluctuations during the first few days, the current density was 0.77 A/m^2 of concrete surface.

Treatment Parameters

The treatment was continued for a period of eight weeks. The fiber was sprayed with water daily to minimize the circuit resistance. The rectifier output was limited to a nominal value of 40 V.

During treatment, the following measurements were made:

- The voltage and current at the rectifier were measured daily.
- The potentials of the embedded reference electrodes were measured periodically.

- The chloride concentration of the electrolyte was also measured periodically. Since some of the electrolyte drained away, these measurements were used only to provide an indication of the progress of the chloride removal.
- Cores were taken after three, seven, and eight weeks to establish the chloride ion profiles in the concrete.

After treatment, the following actions were taken:

- Potentials of the embedded reference electrodes were measured periodically.
- Surface corrosion potentials and rate-of-corrosion measurements were made six weeks, six months, and thirteen months after treatment. Surface corrosion potentials were also measured ten months after treatment.
- Cores were taken six weeks after treatment for petrographic examination.

RESULTS

Appearance

The cellulose was light brown in color and, immediately after installation, was unobtrusive. After 24 hours a rust-stained outline of the mesh was visible and within about three weeks the cellulose had a fairly uniform red-brown appearance as the result of corrosion of the mesh, as shown in Figure 3. The excess water which drained from the cellulose following the daily wetting also contained rust

which stained the column plinth. After the eight weeks of treatment, the surface of the column and parts of the plinth were heavily stained by rust. The staining was removed by blast cleaning.

Power Requirements

The voltage and current throughout the treatment period are shown in Figure 4. The voltage and current fluctuated during the first three days. During the remainder of the eight weeks, there was a slight increase in voltage, but a substantial decrease in current to about one-third its initial value. The total charge passed was approximately 610 A.h/m² of concrete surface.

The power level used was not sufficient to heat the concrete. There was no measurable difference between thermocouples embedded at the level of the steel in the south and north faces.

Chloride Ion Content

Typical chloride ion profiles at various stages in the treatment process are shown in Figure 5. The profiles were established by cutting cores into 10 mm thick slices, pulverizing each slice, and measuring the acid-soluble chloride ion content. Because the flow of drainage water over the column was uneven, the initial chloride ion content of the concrete varied considerably over each face. In order to minimize these variations and permit a valid comparison of the progress of the desalination, cores were taken vertically below each other on each face. Two sets of cores were taken on the west face, one set directly over a vertical reinforcing bar and the other set midway between adjacent vertical bars.

All the results exhibited a similar pattern: chloride ion reduction was most rapid in the early stages of treatment, there was a reduction in the peak chloride ion content and a gradual shift in the peak value towards the concrete surface, and there was little difference between the results after seven and eight weeks. In all cases, the chloride ion content at the level of the reinforcement was at or slightly below the calculated corrosion threshold value for the concrete. By comparing Figures 5(b) and 5(c), it can be seen that proximity to the reinforcement had only a small effect, though the use of 100 mm diameter cores would tend to mask differences in the immediate vicinity of the reinforcement.

The proportion of chloride ion in excess of the corrosion threshold value removed by the treatment was calculated from the area under the curves in the chloride ion profiles. The results are given in Table 1. The range represents the values calculated after seven and eight weeks. In some cases, as for example in Figures 5(b) and (c), the values were less after seven weeks than eight weeks, though this is thought to be the result of the method of sampling.

Corrosion Potential Measurements

The potential of the embedded reference electrodes was measured periodically and the rate of depolarization is shown for the case of the west face in Figure 6. Measurements were made on an embedded graphite electrode. The original static potential was reached after about sixty days. The steel continued to depolarize and zero potential was measured about eight months after treatments. This value was confirmed by surface measurements.

The first set of surface potential measurements were made six weeks after treatment because of the impending onset of winter, but the values were influenced by the fact that the reinforcement had not completely depolarized. Additional readings were taken six, ten, and thirteen months after treatment when the air temperature was 15°C, 27°C, and 12°C respectively The percentage of readings falling within each of the three ranges normally associated with passive, uncertain, and active corrosion activity is given in Table 2. The potential measurements for the treated faces were sensibly the same at six months and later ages, and indicated a substantial reduction in corrosion activity. However, the potential measurements taken on the untreated north face also showed a shift in the positive direction, which fluctuated with time and temperature.

Corrosion Current Measurements

The corrosion currents were measured using a commercial three-electrode linear polarization device. The results six weeks, six months, and thirteen months after treatment are summarized in Table 3 and show a substantial reduction in corrosion activity. The average values recorded on the north face exhibit the fluctuation commonly observed on reinforced concrete structures.

Petrographic Examination

Two cores, 120 mm in diameter, were examined petrographically by Lankard Materials Laboratory Inc., in order to apply the same techniques as were developed for use in SHRP Contract C-102A. One core was taken from the east face and the other from the untreated north face. Both cores contained a No. 11 rebar about 100 mm from the surface.

The cores were subjected to the following tests: a petrographic examination on lapped and fracture surfaces; scanning electron microscopy (SEM) on fracture surfaces; energy dispersive X-ray analyses (EDS) to provide elemental chemical analyses on mortar fracture surfaces; and mercury porosimetry on mortar taken from adjacent to the rebar to determine pore volume and distribution.

The concrete was assessed to be of good quality and no features of mechanical or chemical distress which could be attributed to the electrochemical treatment were observed in the petrographic examination.

The results of the SEM and EDS examinations on samples removed from the top 75 mm of the cores indicated that the electrochemical treatment had no significant effect on the concrete chemistry or microstructure other than the intended purpose of reducing the chloride ion concentration. In the electrochemically treated concrete, a slight discoloration of the concrete adjacent to the rebar was observed, but the paste and aggregate were judged to be of the same quality as the other sites examined in the core. A redistribution of potassium ions occurred in the treated concrete and high levels were found in isolated pockets of mortar within 6 mm of the rebar. It is likely that the concentration of sodium ions also increased at these locations. The porosity of the cement paste phase was 25 to 30 percent higher in the treated concrete, though the increased porosity was primarily in the pore size range less than 1 micron and was not expected to have a significant effect on the permeability of the concrete.

It was concluded that the electrochemical treatment had not had an adverse effect on the concrete at the time of examination. There was no evidence of cracking or softening of the concrete as a result of the treatment (7).

DISCUSSION

The electrochemical treatment removed a large proportion of the chloride ions from the concrete without apparent damage to the pier and with only minor effects on the microstructure of the concrete. The progress of the removal was much as anticipated; relatively rapid at first with a noticeable decline in efficiency as the circuit resistance increased and the transference number decreased. The transference number, t_{Cl}, where $t_{Cl} = \frac{Q_{Cl}}{Q_{TOTAL}}$ represents the quantity of electricity carried by the chloride ions as a proportion of the total quantity passed. The transference number is directly related to the chloride concentration but is independent of current density and only slightly affected by temperature (5). While no attempt was made to determine the optimum treatment time, there was little change in the chloride ion profiles between seven and eight weeks. Treatment times could be reduced by increasing the current density though this would have required a larger power source and increased the risk of damage to the concrete. The current density on the concrete decreased from an initial value of 0.77 A/m^2 to 0.26 A/m^2 after approximately six weeks with the result that the operating current density was substantially less than the 2 A/m^2 suggested as the upper limit for treatment without damage to the concrete (5).

The corrosion potential measurements and, more particularly, the rate-of-corrosion measurements indicated that the corrosion activity had been sub-

stantially reduced. These measurements were consistent with the chloride ion contents measured at the level of the reinforcement. However, a change in corrosion activity would be expected as a result of the large degree of polarization of the steel and three major questions which will determine the technical and economic feasibility of the method remain to be answered:

i) For how long is the treatment effective?

ii) What happens to the chloride ions which remain in the concrete?

iii) What happens to the chloride ions in the corrosion products and pits in the reinforcement?

The answer to the first question requires long term monitoring which is planned for Pier S19 at Burlington. If the treatment was used as a routine operational procedure, it would be expected that, as a minimum, the surface of the concrete would be sealed against further ingress of chloride ions. Since the application procedures for most concrete sealers require that the surface be prepared by blast cleaning, the rust staining associated with the use of the steel mesh anode is not considered a major disadvantage compared with the use of an inert anode. The surface of the concrete in this project was not sealed because the source of the chloride ions has been eliminated as the result of the construction of a new bridge deck in 1988 which was continuous over Pier S19. This will enable changes in the pier to be monitored without the complicating factor of the role of a sealer. In the longer term, it is possible that the service life of chloride ion removal treatments will be extended by the migration of cationic corrosion inhibitors into the concrete, either concurrently with the removal process or as a separate post-treatment.

While the treatment removed a substantial proportion of the chloride ions from the concrete, 13 to 58 percent of the original chloride ion content in excess of the threshold for corrosion remained in the concrete at the conclusion of the treatment. The reason for the much lower proportion of chloride ions removed from the east face is uncertain because the current density applied to each of the treated faces was sensibly the same. Although chloride ion measurements indicated that the value at the reinforcing steel were at or below the anticipated threshold value for corrosion, the EDS analyses detected chloride ions at the concrete-rebar interface and in close proximity to the rebar in the treated concrete. However, the chloride ions were associated with sulphur and aluminum ions and may have been chemically combined as chloroaluminates or chlorosulfoaluminates. The biggest unknowns are then the extent to which chloride ions contained in the steel corrosion products and in the concrete will initiate further corrosion and the period of time during which this may happen, since these factors determine the practicality of the process. In the case of Pier S19, the chloride ion content below the reinforcing steel was quite low, but in a heavily contaminated member, the ability of the process to remove chloride ion from behind the reinforcing steel would also require investigation. This situation is likely to represent the more typical case because of the large amount of cover in Pier S19.

In addition to the above uncertainties, additional work is required to define optimum treatment parameters, particularly with respect to zone area, current density, and time. However, even with optimization, treatment times are likely to be weeks rather than days, making the process more suitable for application to substructure components than decks. Finally, the costs of the treatment have

not been well established. Mobilization and the requirement for daily wetting and periodic monitoring have a major impact on the cost of small scale field trials. There has been insufficient experience to determine reliable costs for full scale applications, but the costs are expected to be competitive with other rehabilitation methods providing that electrochemical removal will offer a similar extension of service life.

CONCLUSIONS

1. Chloride ions were moved away from the reinforcing steel and a significant proportion were removed from the concrete without apparent mechanical or chemical damage to the concrete.
2. The corrosion activity of the steel was reduced substantially.
3. The long term effectiveness of the treatment is the major unknown factor.

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Table 1: Percentage of Chloride Ion Removed by Treatment

FACE	LOCATION	% Cl^- REMOVED
West	Over rebar Between rebars	76-87 74-77
South	Between rebars	65-79
East	Between rebars	42-55

Table 2: Corrosion Potential Measurements

CORROSION POTENTIALS (Mv vs $Cu-CuSO_4$, negative sign omitted)

	NORTH			WEST			SOUTH			EAST		
	<200	200 to 350	>350	<200	200 to 350	>350	<200	200 to 350	>350	<200	200 to 350	>350
Original	0	85	15	0	96	4	0	96	4	0	84	16
6 weeks after treatment	0	81	19	38	42	20	22	33	45	29	31	40
6 months after treatment	63	37	0	96	4	0	100	0	0	98	2	0
10 months after treatment	30	70	0	96	4	0	100	0	0	98	2	0
13 months after treatment	41	59	0	98	2	0	100	0	0	100	0	0

Table 3: Corrosion Current Measurements

AVERAGE CORROSION CURRENTS in $\mu A/cm^2$

	NORTH	WEST	SOUTH	EAST
Before	1.24	0.71	0.60	1.61
6 weeks after treatment	0.90	0.15	0.11	0.16
6 months after treatment	0.81	0.22	0.10	0.17
13 months after treatment	1.24	0.15	0.10	0.18

Figure 1: Application of the First Layer of Cellulose

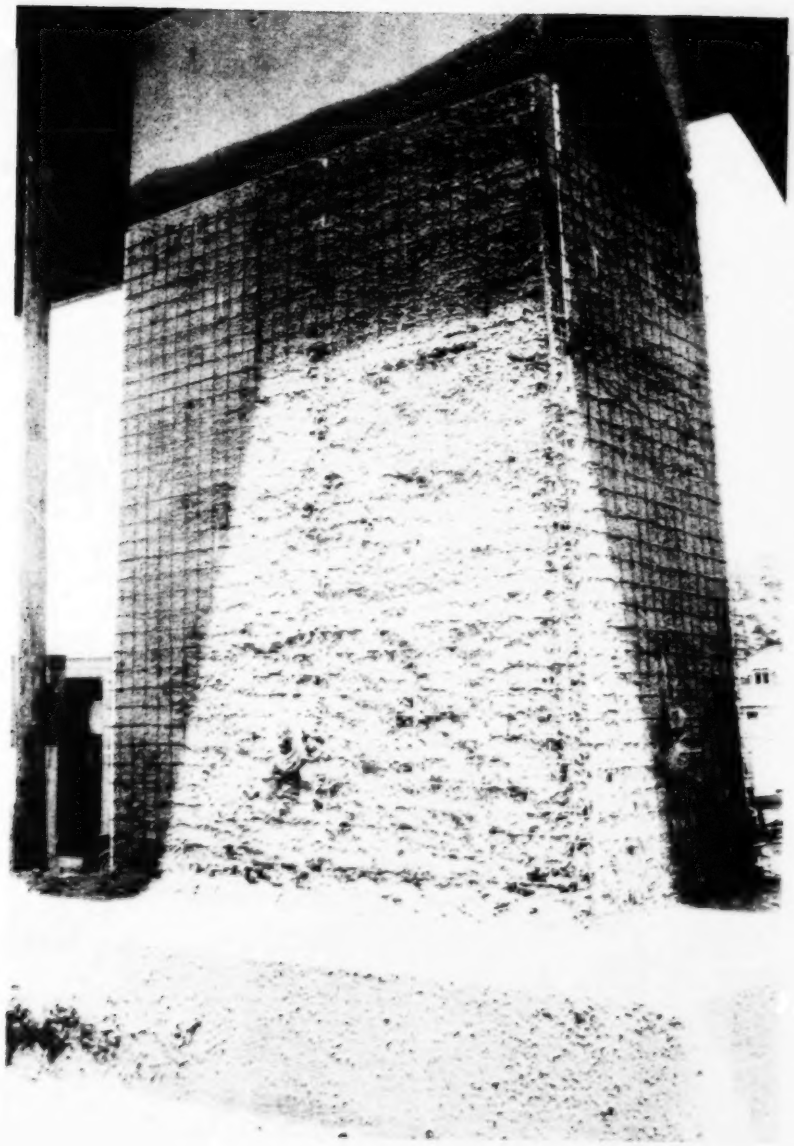

Figure 2: The West and South Faces Prior to Application of the Second Layer of Cellulose

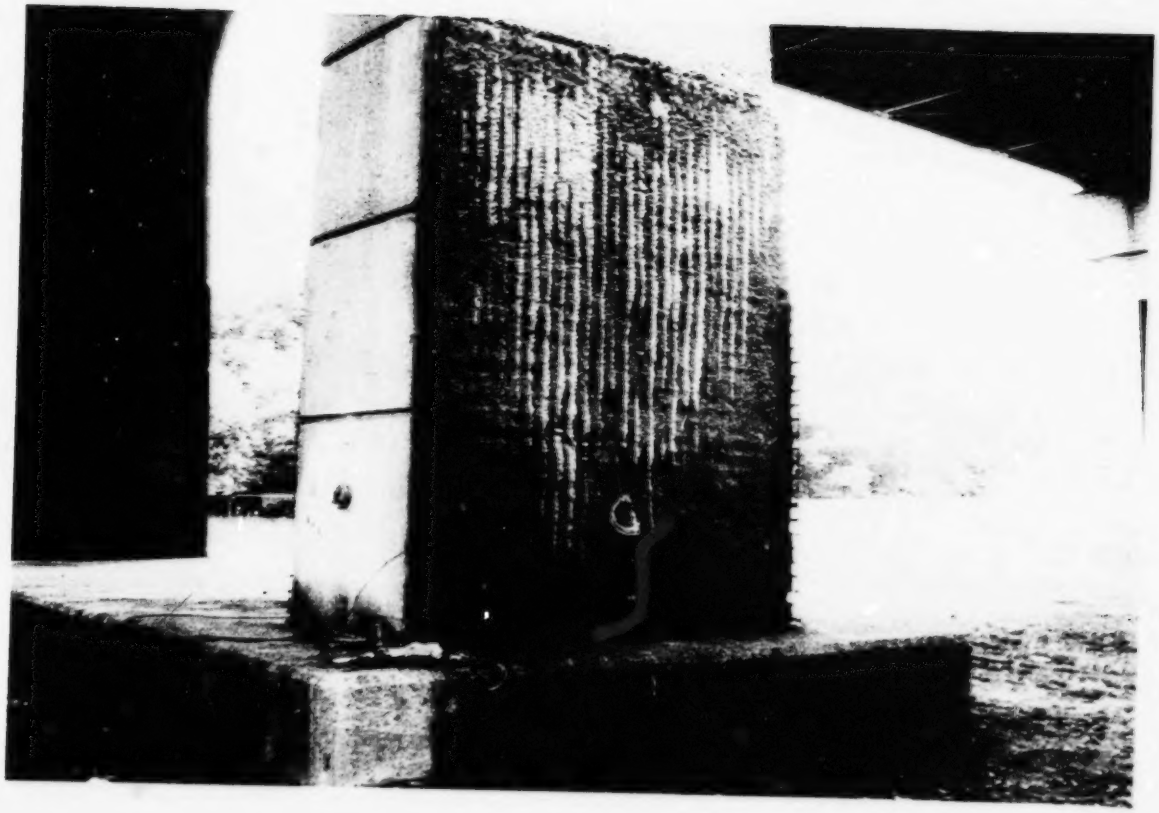

Figure 3: Rust-Staining of the Cellulose on the West Face After Three Weeks of Treatment

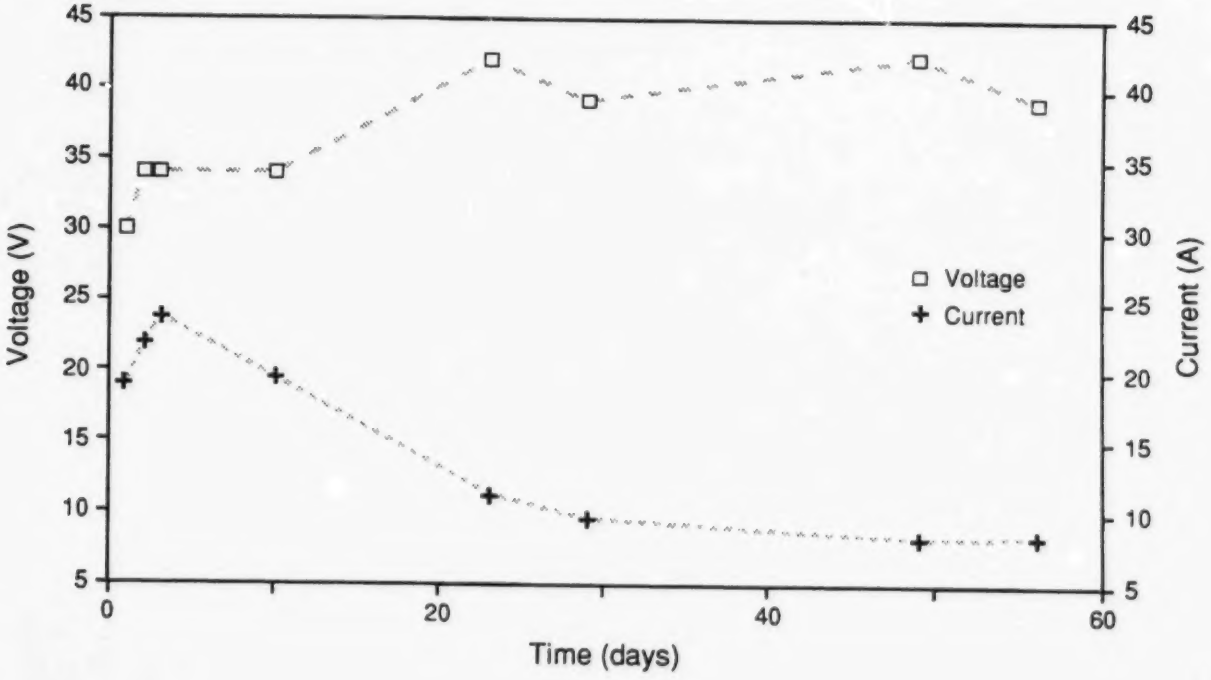

Figure 4: Rectifier Output During Treatment Period

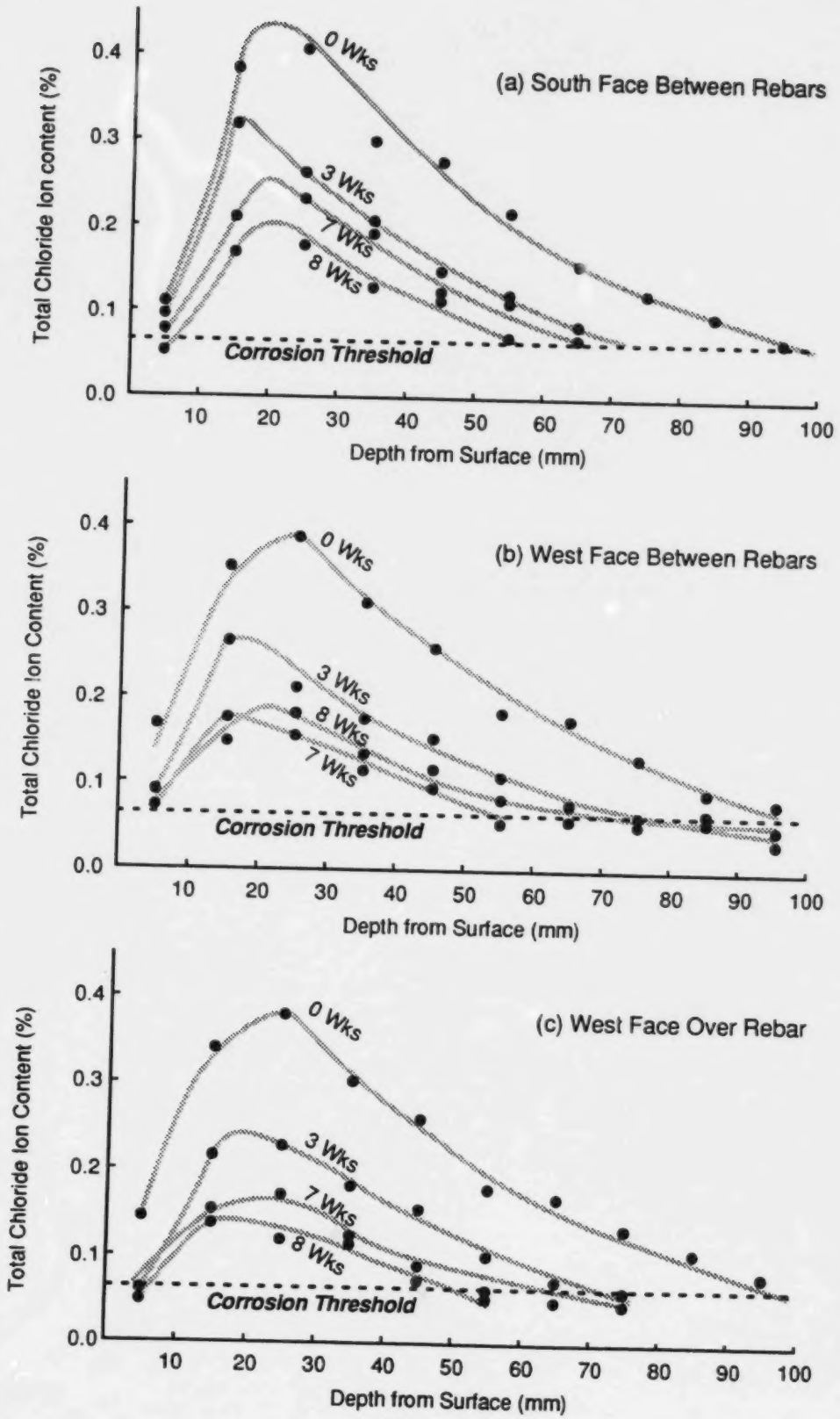

Figure 5: Chloride Ion Profiles During Treatment Period

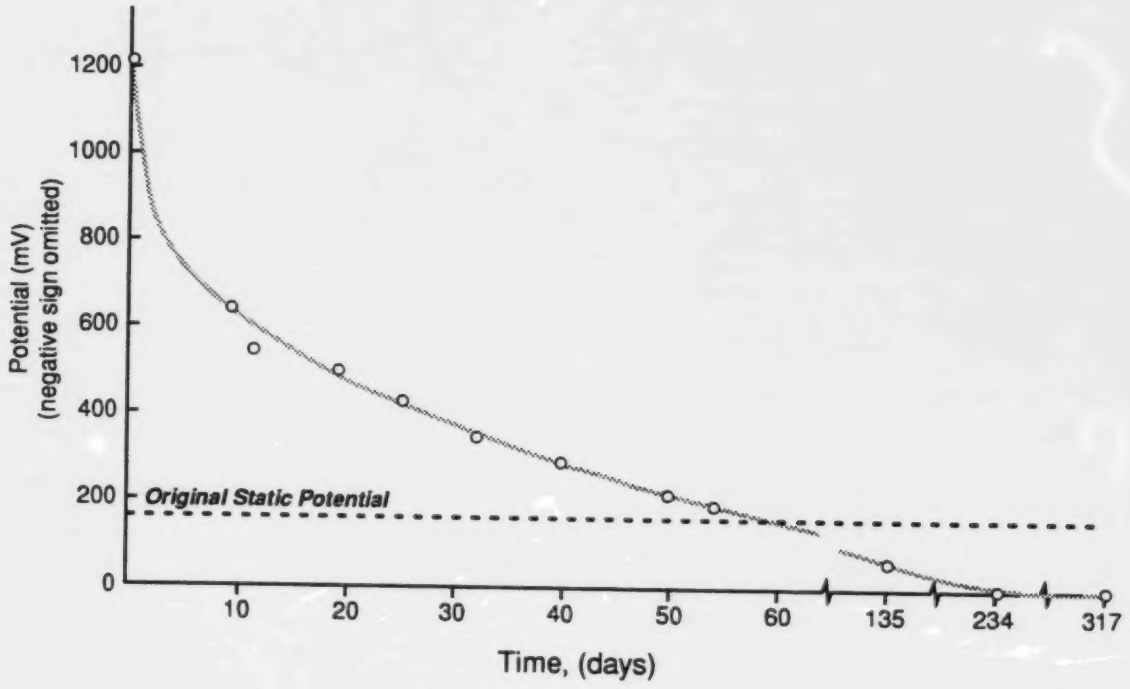

Figure 6: Depolarization of the West Face Measured on an Embedded Graphite Electrode